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(54) **Surfactant treated polyolefinic microporous materials capable of multiple re-wetting with aqueous solutions.**

(57) Hydrophilic polyolefinic microporous materials are prepared by impregnating a normally hydrophobic polyolefinic microporous substrate material with a solution of a non-ionic alkylophenoxy poly (ethyleneoxy) ethanol surfactant having an HLB of 10 to 15 in a solvent system comprising 55 to 65 volume percent methanol or acetone and 35 to 45 volume percent water. Polyolefinic microporous materials rendered hydrophilic by this technique not only wet rapidly, but in addition may be multiply re-wet with aqueous solutions, such as aqueous alkali solutions, with excellent retention of their hydrophilic properties. Such materials find particular application as battery separators and an membranes for use in various chemical, medical and biotechnical processes.

SURFACTANT TREATED POLYOLEFINIC  
MICROPOROUS MATERIALS CAPABLE OF  
MULTIPLE RE-WETTING WITH AQUEOUS  
SOLUTIONS

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The present invention relates to a hydrophilic polyolefinic microporous material.

The material may be a hydrophilic microporous membrane, of the type wherein a normally hydrophobic polyolefinic microporous material is impregnated with a surfactant in order to impart hydrophilic properties, such as water permeability, to the material. The present invention particularly relates to hydrophilic microporous materials of the aforementioned type which are rapidly wettable, particularly by aqueous solutions, and in addition may be multiply re-wet, i.e., re-used, without significant surfactant wash-out and an attendant loss of hydrophilic properties of the material upon re-wetting.

Polyolefinic microporous materials, for example polyolefinic microporous films and hollow fibres, are well known to those skilled in the art (see, for example, U.S. Patents Nos: 4,020,230; 4,055,696; 4,290,987; 3,839,516; 3,801,404; 3,679,538; 3,558,764 and 3,426,754). Due to the advantageous properties of these materials, such as chemical inertness and stability, physiological compatibility and safety, as well as the unique porous structure thereof, polyolefinic microporous films and hollow fibres have found utility in a wide variety of applications such as gas-breathing water barriers, gas-liquid transfer mediums and membranes for use in blood oxygenation and in various separation processes.

One disadvantage of the polyolefinic microporous membranes which in the past has limited the number of applications in which these materials may be utilised has been their hydrophobic nature. Due to this hydrophobic nature, despite their other desirable physical characteristics, the polyolefinic microporous membranes have not been readily usable in those applications which require an aqueous permeable and/or wettable membrane, such as, for example, battery separators and membranes for use in blood plasmapheresis.

One approach to this problem has been to treat the normally hydrophobic polyolefinic microporous material with various surfactants in order to impart hydrophilic characteristics such as water-permeability and wettability thereto.

5 U.S. Patent No: 3,853,601, for example, discloses polyolefinic microporous films such as polypropylene microporous films, which are rendered hydrophilic by treatment with a silicon glycol copolymeric surfactant. In other embodiments, the microporous film may be impregnated with a combination of  
10 a silicon glycol copolymeric surfactant and a cationic imidazoline tertiary amine. The disclosed surfactants are applied to the exemplified polyolefinic microporous films by contacting the film with a dilute solution of about 1 to 10% by weight of the surfactant and/or surfactants in an  
15 organic solvent such as acetone, methanol, ethanol or isopropyl in order to produce an "add-on" of the surfactant to the microporous film of about 2 to about 20 percent by weight, based on the weight of the uncoated microporous film. Hydrophilic microporous polyolefinic films produced  
20 by this method are described as being rapidly wettable and useful as battery separators.

Similarly, U.S. Patent No: 4,290,987 teaches that polyolefinic microporous hollow fibres may be rendered hydrophilic by treatment with surfactants such as polyvinylpyrrolidone (PVP), various high molecular weight condensation  
25 products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol (e.g., the Pluronics), and various polyoxyalkylene derivatives of hexitol anhydride partial long chain fatty acid  
30 esters (e.g., the Tweens). (Pluronic and Tween are Trade Marks).

In addition to the foregoing surfactants, a variety of other surfactants have also been examined for use in rendering polyolefinic microporous materials hydrophilic. U.S.  
35 Patent No: 4,298,666, for example, describes the use of phosphate esters such as ethoxylated 2-ethylhexyl phosphate in the treatment of polyolefinic microporous films.

A wide variety of other surfactants which have heretofore been employed in order to improve the hydrophilic characteristics of polyolefinic films are further described in Canadian Patent No: 981,991; they include hexachlorophene  
5 modified soaps, polypropoxylated quaternary ammonium chlorides, organic phosphate esters, imidazolines, fatty acids and their alkali metal salts and various fatty and alkali amines.

Wettable polypropylene non-woven mats, suitable for use  
10 as battery separators, have also been proposed in the prior art. U.S. Patent No: 3,947,537, for example, describes non-woven polypropylene mats having a pore size of less than 25 microns and a porosity in excess of 50% which are rendered wettable by impregnation with about 0.3 to 1.0 per-  
15 cent by weight of an anionic surfactant such as sodium dioctylsulfosuccinate or non-ionic polyoxyethylene oxy compounds such as nonylphenoxy poly(ethyleneoxy) ethanol (i.e. Igepal CO-730) or alkylaryl polyether alcohol compounds. (Igepal is a Trade Mark).

20 Similar battery separators of the porous non-woven mat type are also disclosed in U.S. Patents Nos: 3,870,567; 3,918,995 and 3,933,525. In each of these Patents the non-woven mats are prepared from polypropylene fibres containing a wetting agent system that is insoluble in battery electro-  
25 lytes and tends to bloom (i.e., rise to the surface of the polypropylene fibres) under conditions of use. In the preferred embodiment, the wetting agent system comprises a first non-ionic wetting agent having an HLB (Hydrophilic Lipophilic Balance) number less than 5, and a second wetting  
30 agent having an HLB greater than 5 selected from non-ionic and anionic surfactants. Specifically exemplified surfactants include, inter alia, the ethoxylated adducts of polypropylene oxide with propylene glycol (Pluronic L-121), nonylphenol ethylene oxide adducts such as Tergitol NP-14, TP-9, NP-33  
35 and NP-44; dodecylphenol ethylene oxide adducts such as Tergitol 12-P-5 and 12-P-6 and alkylaryl polyethers such as Triton X-100, as well as a variety of other surfactants based on ethylene oxide. (Tergitol and Triton are Trade Marks).

While the above-described hydrophilic polyolefinic materials are wettable, in varying degrees, with aqueous liquids and are thus suitable for some purposes, the surfactant impregnated polyolefinic materials of the prior art have in general exhibited less than desirable retention of their hydrophilic properties upon repeated use. It has been observed with these systems that many of the surfactants employed therein have a relatively low adhesion to the polyolefinic material, and upon repeated use tend to be washed-out from the polyolefinic material with an attendant loss in the hydrophilic and wettability properties of the polyolefinic material. In battery separator applications, for example, the long-term bathing and agitation of the polyolefinic separators by the battery electrolyte produces surfactant wash-out, with a resulting increase in internal electrical resistance as the life of the battery increases. Similarly, in applications such as plasmapheresis (as well as in other filtration processes) passage of the blood plasma (or other liquid to be filtered) through the polyolefinic microporous membrane tends to wash-out the surfactant, with the result that the efficiency of the microporous polyolefinic membrane decreases precipitously with time.

Recently hydrophilic microporous polyolefinic films have also been developed wherein the water wettability and water-permeability properties of the hydrophobic polyolefinic material are improved by grafting the polyolefinic material with a controlled amount of a hydrophilic monomer such as acrylic acid in the presence of a controlled dosage of ionising radiation (see, e.g., U.S. Patent No: 4,346,142). Hydrophilic microporous polyolefinic films prepared by the technique disclosed in this Patent, due to the chemical attachment of the hydrophilic monomer to the polyolefinic material, do not exhibit transient water-permeability properties and thus comprise highly desirable hydrophilic membrane materials. Due to their convenience, it would nonetheless be desirable to provide hydrophilic microporous polyolefinic materials of the surfactant impregnated type having improved surfactant retention and re-wettability properties.

Accordingly, it is an object of the present invention to provide an improved hydrophilic microporous polyolefinic material of the surfactant impregnated type. The invention provides such a material with a number of surprising advantages.

In accordance with the present invention there is provided a hydrophilic polyolefinic microporous material which comprises a normally hydrophobic polyolefinic open-celled microporous material impregnated with at least one non-ionic alkylphenoxy poly(ethyleneoxy) ethanol surfactant having an HLB (Hydrophilic Lipophilic Balance) number in the range of 12 to 15 in an amount sufficient to render the normally hydrophobic material aqueous solution wettable.

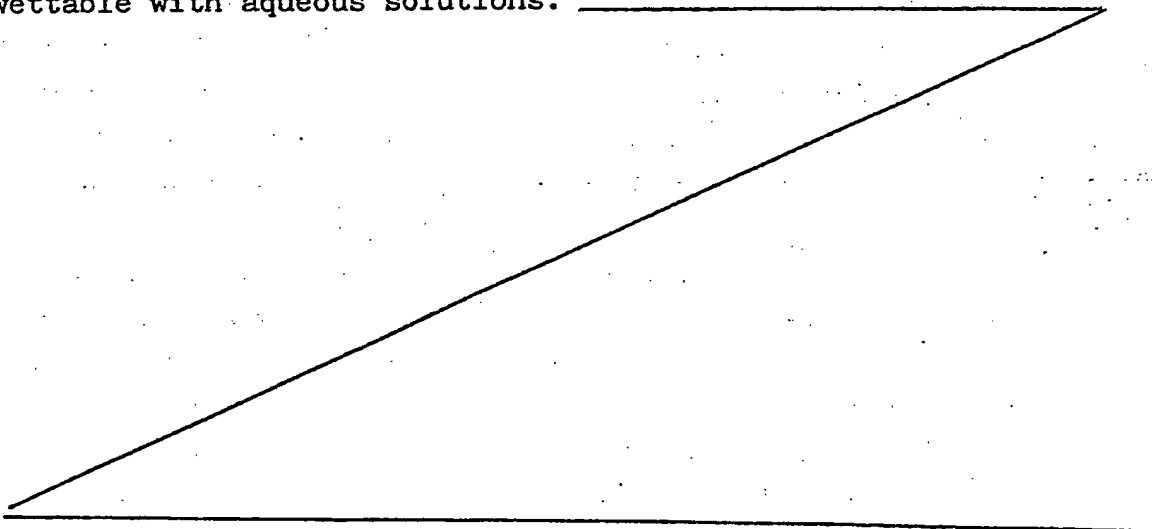
Among the surprising advantages provided by the present invention are the following.

The material exhibits not only low electrical resistance in aqueous medium, excellent wettability and water permeability, but in addition improved retention of these properties during use.

The invention also provides a process for preparing a hydrophilic microporous polyolefinic material of the surfactant impregnated type having the combination of properties mentioned above.

Preferred hydrophilic polyolefinic microporous materials within the scope of this invention are prepared by impregnating the normally hydrophobic polyolefinic microporous material with a surfactant solution comprising at least one of the aforementioned alkylphenoxy poly(ethyleneoxy) ethanol surfactants in a solvent system comprising a mixture of 55 to 65 volume percent (most preferably about 60 volume percent) of methanol or acetone with 35 to 45 volume per cent (most preferably about 40%) of water. The concentration of the surfactant solution, contact time and surfactant add-on are all chosen so as to render the normally hydrophobic polyolefinic microporous material wettable with aqueous solutions.

It has been surprisingly discovered that, in contrast to the more common surfactant-coated microporous materials of the prior art, the hydrophilic polyolefinic microporous materials prepared by the techniques of this invention possess not only excellent wettability with aqueous solutions but in addition exhibit an improved retention of their hydrophilic properties, as demonstrated by their ability to be multiply re-wet with aqueous medium. This latter advantage is believed to be due not only to the particular class of surfactants employed herein but also to the impregnation procedure utilised in the preparation of the hydrophilic polyolefinic microporous materials of this invention. In other embodiments, therefore, the present invention thus also provides a method for the preparation of hydrophilic polyolefinic microporous materials having improved wettability and retention of wettability properties which comprises contacting a normally hydrophobic polyolefinic microporous material with a solution of at least one non-ionic alkylphenoxy poly(ethylenoxy) ethanol surfactant having an HLB in the range of 10 to 15 in a solvent mixture comprising 55 to 65 volume percent methanol or acetone and 35 to 45 volume percent of water in a manner sufficient to render said normally hydrophobic polyolefinic microporous material wettable with aqueous solutions.



The present invention further provides hydrophilic polyolefinic microporous materials having improved wettability and retention of hydrophilic properties which are prepared by the aforementioned method.

5 Other features and advantages of the present invention, as well as the preferred modes of operation thereof, will become apparent from the following detailed description of the preferred embodiments.

The present invention is based upon the discovery that  
10 the class of alkylphenoxy poly(ethyleneoxy) ethanol surfactants having an HLB in the range of 10 to 15 comprise unusually good surfactants for use in the preparation of hydrophilic polyolefinic microporous materials, providing hydrophilic polyolefinic microporous materials having excellent  
15 wettability characteristics. It has been further discovered that the adhesion of the aforementioned surfactants to the polyolefinic microporous material is improved by impregnating the polyolefinic microporous material with the surfactant in the form of surfactant solution containing as the solvent  
20 from 55 to 65 volume per cent methanol or acetone and from 35 to 45 volume percent of water. Best results are obtained with a solvent mixture comprising about 60 volume percent of acetone or methanol and about 40 volume percent of water. When applied to the polyolefinic microporous material by  
25 this technique, the aforementioned alkylphenoxy poly(ethyleneoxy) ethanol surfactants exhibit strong adhesion to the polyolefinic microporous materials and provide hydrophilic polyolefinic membranes having improved retention of their hydrophilic properties, as demonstrated by their ability  
30 to be multiply re-wet with aqueous media.

As a result of these significant advantageous properties, the hydrophilic polyolefinic microporous materials of this invention are highly desirable for use as membranes in environments wherein hydrophilic properties are required,  
35 for example as membranes for use in separation and filtration processes such as, e.g., plasmapheresis. In addition, the chemical resistance provided by polyolefin membranes together with the advantageous wettability characteristics of the



surfactant treated membranes of this invention make such membranes ideal materials for use as battery separators. Battery separators prepared from the microporous membranes of this invention typically exhibit, for example, an  
5 electrical resistance of less than 15 milliohms-in.<sup>2</sup>, and more usually less than 10 milliohms-in.<sup>2</sup>, as measured by the technique described in U.S. Patent No: 4,298,666.

The alkylphenoxy poly(ethyleneoxy) ethanol surfactants employed in the hydrophilic polyolefinic microporous  
10 materials of this invention, as mentioned above, possess an HLB (Hydrophilic Lipophilic Balance) from 10 to 15. Such surfactants are well known to those skilled in the art, and are readily commercially available. Suitable surfactants include, for example, the 500 and 600 series compounds sold  
15 under the trade name Igepal by the GAF Corporation, such as Igepal RC-520, RC-620, RC-630, CO-520, CO-530, CO-610, CO-630, CO-660, CO-720, CA-520, CA-620 and CA-630. Preferred alkylphenoxy poly(ethyleneoxy) ethanol surfactants for use in the hydrophilic polyolefinic microporous materials  
20 of this invention have an HLB of 12 to 13, such as, for example, Igepal RC-620, RC-630, CO-610, CO-630, CO-660, CA-620 and CA-630, of which Igepal CO-610, CO-630 and RC-630 have been found to give particularly good results.

The polyolefinic microporous materials rendered hydro-  
25 philic with the above surfactants may comprise any suitable polyolefinic microporous material well known in the art. Generally, the polyolefinic microporous material will be in the form of a flat film or sheet or hollow fibre, but may in addition be in any other configuration known to those skilled  
30 in the art such as hollow tubes, fabrics, laminates etc. Examples of suitable microporous materials are disclosed for instance in U.S. Patents Nos: 4,020,230; 4,055,696; 4,290,987; 3,839,516; 3,801,404; 3,679,538; 3,558,764 and 3,426,754.

35 The microporous membranes employed herein may also comprise any suitable polyolefin well known to those skilled in the art. Illustrative examples of suitable polyolefins

include polyethylene, polypropylene, poly-3-methyl butene-1, poly-4-methyl pentene-1, copolymers of ethylene, propylene, 3-methyl butene-1, or 4-methyl pentene-1 with each other or with minor amounts of other olefins, e.g., copolymers of  
5 ethylene and propylene, copolymers of a major amount of 3-methyl butene-1 and a minor amount of a straight chain n-alkene having from 2 to 18 carbon atoms such as n-octene-1, n-hexadecene-1, n-octadecene-1 or other relatively long chain alkenes, as well as copolymers of 3-methyl pentene-1  
10 and any of the same n-alkenes mentioned previously in connection with 3-methyl butene-1. The polyolefinic material may also include small amounts (e.g., less than 20% by weight) of other materials which may be copolymerised or blended therewith, but which do not substantially adversely  
15 affect the characteristics of the polyolefinic material. A particularly preferred polyolefin is isotactic polypropylene having a weight average molecular weight in the range from 50,000 to 600,000, preferably from 100,000 to 600,000; and a melt index in the range from 0.6 to 35, preferably from  
20 0.6 to 15, and most preferably from 0.6 to 8 (e.g., from 1 to 5).

Also particularly preferred is high density polyethylene having a density greater than 0.960; a weight average molecular weight from 50,000 to 600,000, preferably from  
25 100,000 to 600,000; and a melt index from 0.5 to 15, preferably from 0.6 to 8 and most preferably from 0.6 to 5.

Preferred polyolefinic microporous materials for use in preparing the hydrophilic membranes of this invention are of the open-celled type, i.e., of the type in which the pores  
30 are essentially interconnected through tortuous paths which may extend from one exterior surface or surface region to another. Such preferred membranes also exhibit a reduced bulk density as compared with the density of the corresponding non-porous structures from which they are made; a crystallin-  
35 ity of at least 30 percent, more preferably from 50 to 100 percent, as determined by the X-ray method described by

R.G.Quynn et al in the Journal of Applied Polymer Science, Vol. 2, No. 5, pp. 166-173 (1959); an average pore size of from 100 to 12,000 Angstroms (preferably from 100 to 5,000 Angstroms); a surface area of at least  $10\text{m}^2/\text{g}$  (preferably from 20 to  $100\text{m}^2/\text{g}$ ), as measured by the BET method, which is described in detail in the Journal of the American Chemical Society, Vol. 60, pp. 309-316 (1938); and a porosity of from 40 to 90% as measured by mercury porosimetry.

10 Preferred polyolefinic microporous membranes for use in this invention are further characterised by an oxygen flux of at least 10, preferably in the range from 30 to 300 and most preferably in the range from 100 to  $300\text{cc}/\text{cm}^2\text{min}$  at 10 psi. The oxygen flux,  $J_g$ , of a microporous membrane is  
15 a measure of its effective permeability, and is determined by passing oxygen gas through a sample of microporous membrane at a pressure of 10 psi and collecting the same. The volume of the gas collected over a period of time is then used to calculate the gas flux in  $\text{cc}/\text{cm}^2\text{min}$  of the sample  
20 of microporous membrane according to the equation:

$$J_g = \frac{V}{(A)(T)}$$

wherein V is the volume of gas collected; A is the surface area of the microporous membrane (for hollow fibre membranes A is the internal surface area of the hollow fibre); and T  
25 is the time in minutes it takes to collect the gas.

As mentioned above, the microporous membranes preferred for use in the preparation of the hydrophilic polyolefinic microporous membranes of the invention exhibit a reduced bulk density. That is, these membranes have a bulk or  
30 overall density lower than the bulk density of corresponding membranes composed of identical polymeric material but having no open-celled or other voidy structure. The term "bulk density" as used herein means the weight per unit of gross or geometric volume of the membrane, where gross volume is  
35 determined by immersing a known weight of the film in a

vessel partly filled with mercury at 25°C. and atmospheric pressure. The volumetric rise in the level of mercury is a direct measure of the gross volume. This method is known as the mercury volume-nometer method, and is described in  
5 the Encyclopedia of Chemical Technology, Vol. 4, page 892 (Interscience 1949).

Microporous membranes having the above-described properties have a structure, as shown by various morphological techniques or tests such as electron microscopy, which  
10 is characterised by a plurality of elongated, non-porous, inter-connecting surface regions or areas which have their access of elongation substantially parallel. Substantially alternating with and defined by these non-porous surface regions are a plurality of elongated, porous surface regions  
15 which contain a plurality of parallel fibrils or fibrous threads. These fibrils are connected at each of their ends to the non-porous regions, and are substantially perpendicular to them. Between the fibrils are the pores or open cells of the membranes utilised in the present invention.  
20 These surface pores or open cells are substantially interconnected through tortuous paths or passageways which extend from one surface region to another surface area or region.

With such a defined or organised morphological structure,  
25 the membranes preferred for use herein have a greater proportion of surface area than the pores cover, a greater number of pores, and a more uniform distribution of pores, than other types of microporous membranes. Further, the fibrils present in this type of membrane are more drawn or  
30 oriented with respect to the rest of the polymer material in the membrane, and thus contribute to the higher thermal stability thereof.

Polyolefinic microporous membranes of the above-discussed preferred type are well known to those skilled in  
35 the art, and are available commercially from the Celanese Fibers Marketing Company, Charlotte, North Carolina, under the Trade Mark "Celgard". The preparation of this type of

microporous membrane is also described in, for example, U.S. Patents Nos: 3,801,404; 3,839,516; 3,669,538; 3,801,692; 3,843,761; 3,920,785; 4,138,459; 4,257,997 and 4,290,987, among others. Especially preferred polyolefinic microporous  
5 film membranes for use in the present invention are prepared by the techniques described in U.S. Patents Nos: 3,801,404 and 4,257,997. Preferred polyolefinic microporous hollow fibre membranes are most advantageously prepared by the procedures described in U.S. Patent No: 4,290,987 and in our  
10 U.S. Patent Application Serial No: 349,795, filed February 2, 1982 in the name of James Jay Lowery et al.

The hydrophilic polyolefinic microporous materials of this invention are prepared, as mentioned above, by impregnating the normally hydrophobic polyolefinic microporous  
15 substrate membrane with a solution containing one or more of the aforementioned alkylphenoxy poly(ethyleneoxy) ethanol compounds in a solvent mixture comprising from 55 to 65 volume percent of methanol or acetone and from 35 to 45 volume percent water. Preferably, the solvent system  
20 comprises about 60 volume percent of methanol or acetone (particularly methanol) and about 40 volume percent water. It has been discovered that the use of the aforementioned solvent system achieves a more intimate penetration of the porous structure of the microporous substrate material by  
25 the alkylphenoxy poly(ethyleneoxy) ethanol surfactant than is obtainable by other solvent systems which have been employed for treating microporous materials. As a result of this improved penetration, the surfactant-treated microporous materials of this invention are substantially less  
30 subject to surfactant wash-out, and accordingly exhibit significantly improved retention of their hydrophilic properties, as exemplified by their ability to be multiply re-wet with aqueous solutions. It appears that this enhanced surfactant retention is related not only to the inherent  
35 affinity of the alkylphenoxy poly(ethyleneoxy) ethanol surfactants employed herein to the polyolefinic microporous substrate, but in addition to the solvent system employed

during impregnation, since polyolefinic microporous substrates impregnated using, e.g., an isopropanol/water solvent mixture did not exhibit the superior surfactant retention characteristic of the preferred hydrophilic membranes of this invention.

The surfactant solution utilised during the impregnation procedure preferably is a dilute solution. In the preferred embodiment, the surfactant solution typically comprises from 1 to 10% by weight of one or more of the aforementioned alkylphenoxy poly(ethyleneoxy) ethanol surfactants, more preferably from 5 to 10% by weight of surfactant.

The polyolefinic microporous substrate material may be impregnated by any method well known to those skilled in the art. A preferred procedure comprises simply immersing the microporous substrate material in the surfactant solution for an amount of time sufficient to produce the desired improvement in the hydrophilic properties of the polyolefinic microporous substrate. If desired, the surfactant solution may be employed in the form of an ultrasonic bath, although this procedure does not appear to be critical to the preparation of the hydrophilic materials of this invention.

The amount of surfactant impregnation, i.e., surfactant "add-on", is preferably adjusted in order to provide hydrophilic membranes which are not only surface wet by aqueous solutions but in addition are "wet through" by aqueous solutions. This latter term refers to the ability of aqueous solutions to penetrate and be transported through the polyolefinic substrate material. For the purposes of the present invention, the term "wetable" means that the hydrophilic polyolefinic microporous membrane may be "wet through" by aqueous media. The amount of surfactant add-on required for this purpose varies according to the particular aqueous solution which is desired to wet through the hydrophilic polyolefinic microporous membrane. With alkaline KOH battery electrolyte solutions (comprising from 25 to 45 percent KOH in water), for example, larger amounts of surfactant add-on are often required in order to achieve

"wet through". Generally, surfactant add-ons of at least 5% by weight, based on the weight of the uncoated microporous substrate, are adequate for this purpose. Best results are obtained with surfactant add-ons of from 10 to 15% by weight, and most preferably about 12% by weight. Hydrophilic membranes according to this invention having surfactant add-ons within this range have been found to be still wettable even after six months of use. While add-ons greater than 15% by weight may be employed, if desired, the use of such greater amounts of surfactant add-on has been found to be without advantage, the excess over 15% by weight being washed-out of the membrane during use.

The contact time of the polyolefinic microporous substrate with the surfactant solution during the immersion step is not particularly critical, and is usually adjusted in order to achieve the surfactant add-ons described above. Typical contact times generally comprise from 10 seconds to one hour or more, and will vary according to the concentration of the surfactant solution, the desired add-on, the thickness of the polyolefinic membrane, etc. Suitable contact times may readily be determined given the teachings of this invention by those skilled in the art.

The invention is additionally illustrated by the following Examples. It should be understood, however, that the invention is not limited to the specific details of the Examples.

#### EXAMPLE I

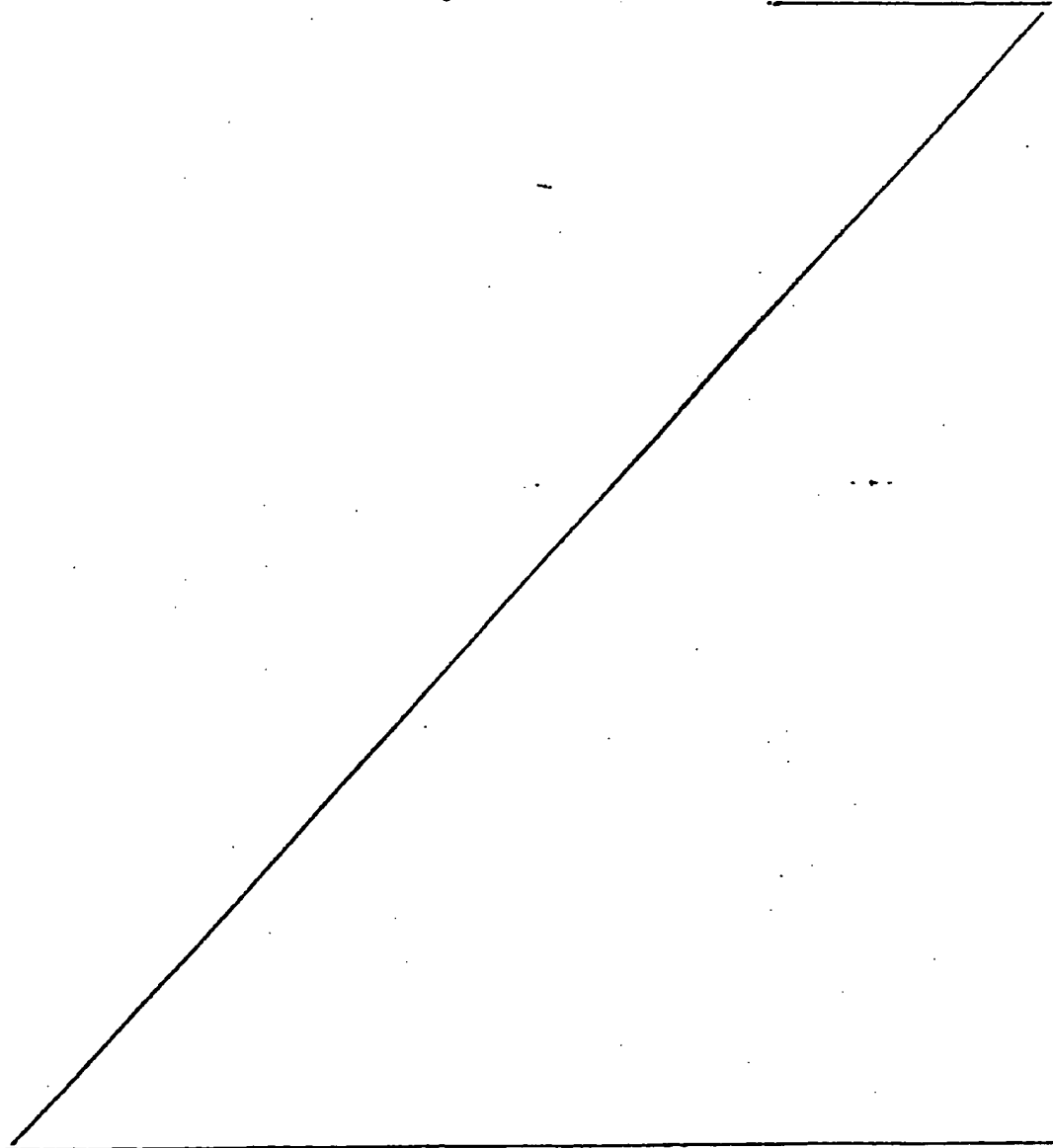
A series of hydrophilic polypropylene microporous hollow fibres were prepared by impregnating Celgard polypropylene microporous hollow fibres with a surfactant solution comprising a 1% by weight solution of the surfactant in a 60/40 methanol-water solvent mixture. In each of these experiments, six two-inch long (5.08 cm long) filaments of polypropylene microporous hollow fibre were cut and attached to a binder clip. The resulting bundle of filaments was then immersed in an ultrasonic bath containing the above-described surfactant solution. After 10 minutes of immersion in the ultrasonic bath the microporous hollow fibre bundle

was removed and allowed to dry. Upon drying the sample was immersed in water to determine wettability. If the sample would wet, it was then re-dried, and the wetting/drying procedure repeated three times to test the re-wettability characteristics of the sample. Celgard is a Trade Mark.

The surfactants employed in these experiments included American Cyanamic Aerosol OT-100 (dioctyl ester of sodium sulfosuccinic acid), IB-45 (diisobutyl ester of sodium sulfosuccinic acid), A-268 (disodium isodecyl sulfosuccinate), OS (sodium isopropyl naphthalene sulfonate) and 18 (disodium N-octadecylsulfosuccinate); BASF Pluronic L-35 (HLB 1.85), L-43 (HLB 12.0), L-101 (HLB 1.0), F-68 (HLB 29.0) and F-108 (HLB 27.0), which comprise condensates of ethylene oxide with hydrophobic bases formed by condensing propylene oxide with propylene glycol; GAF polyvinylpyrrolidone K15, K30, K60 and K90; GAF Igepal CA-520 (octylphenoxy poly(ethyleneoxy) ethanol having an HLB of 10.0), CA-620 (octylphenoxy poly(ethyleneoxy) ethanol having an HLB of 12), CA-630 (octylphenoxy poly(ethyleneoxy) ethanol having an HLB of 13), RC-520 (dodecylphenoxy poly(ethyleneoxy) ethanol), RC-620 (dodecylphenoxy poly(ethyleneoxy) ethanol), RC-630 (dodecylphenoxy poly(ethyleneoxy) ethanol), CO-520 (nonylphenoxy poly(ethyleneoxy) ethanol having an HLB of 10.0), CO-630 (nonylphenoxy poly(ethyleneoxy) ethanol having an HLB of 13.0), CO-660 (nonylphenoxy poly(ethyleneoxy) ethanol having an HLB of 13.2) and CO-720 (nonylphenoxy poly(ethyleneoxy) ethanol having an HLB of 15) and ICI Tween 20 (polyoxyethylene (20) sorbitan monolaurate having an HLB of 16.7), 21 (polyoxyethylene sorbitan laurate having an HLB of 13.3), 40 (polyoxyethylene (20) sorbitan monopalmitate having an HLB of 15.6), 60 (polyoxyethylene (20) sorbitan monostearate having an HLB of 14.9), 80 (polyoxyethylene (20) sorbitan monooleate having an HLB of 15.0), 81 (polyoxyethylene (5) sorbitan monooleate having an HLB of 10.0) and 85 (polyoxyethylene (20) sorbitan trioleate) having an HLB of 11.0).



The results of these experiments are set forth in the Table wherein a "1" signifies wetting of the hollow fibres (measure visually), "0" signifies no wetting of the fibre occurred, and "1/2" signifies partial wetting of the fibre occurred. As mentioned above, microporous hollow fibres found to be either non-wetting ("0") or only partially wetting ("1/2") during the first wetting cycle were not examined for re-wettability characteristics.



TABLE

<u>Surfactant</u>	<u>1st Wetting Cycle</u>	<u>2nd Wetting Cycle</u>	<u>3rd Wetting Cycle</u>
Aerosol OT-100	1/2	-	-
Aerosol IB-45	0	-	-
Aerosol A-268	0	-	-
Aerosol OS	0	-	-
Aerosol 18	0	-	-
Pluronic L-35	0	-	-
Pluronic L-43	0	-	-
Pluronic L-101	1/2	1/2	-
Pluronic F-68	0	-	-
Pluronic F-108	0	-	-
GAF PVP - K15	0	-	-
GAF PVP - K30	0	-	-
GAF PVP - K60	0	-	-
GAF PVP - K90	0	-	-
Igepal RC-520	1	1	1
Igepal RC-620	1	1	1
Igepal RC-630	1	1	1
Igepal CO-520	1	1	1
Igepal CO-630	1	1	1
Igepal CO-660	1	1	1
Igepal CO-720	1	1	1
Igepal CA-520	1	1	1
Igepal CA 620	1	1	1
Igepal CA 630	1	1	1
Tween 20	1	1	1
Tween 21	1	1	1
Tween 40	1	1	1
Tween 60	1	1	1
Tween 80	1	1	1
Tween 81	1	1	1
Tween 85	1	1	1

As can be seen from the Table, hydrophilic polypropylene microporous hollow fibres prepared in accordance with the principles of this invention possess not only excellent wetting characteristics but in addition may be multiply re-wet over a number of wetting/drying cycles, demonstrating an excellent retention of hydrophilic properties upon repeated use. This result is particularly surprising since even when prepared using a 60/40 methanol-water solvent system, polypropylene microporous hollow fibres impregnated with other surfactants which have been suggested for this purpose by the prior art, such as the Pluronic series of surfactants and polyvinylpyrrolidone (c.f. U.S. Patent 4,290,987), possessed only poor wettability and were not capable of being multiply re-wet. In this regard, it is to be noted that while polypropylene microporous hollow fibres impregnated with the Tweens did exhibit desirable wetting characteristics when prepared with a 60/40 methanol-water solvent system, comparable results are not to be expected when the Tweens are impregnated using other solvent systems. As discussed above, it has been found that the substitution of isopropanol for the methanol or acetone component of the solvent system used during impregnation produces microporous materials having inferior re-wetting characteristics. This latter fact further supports the unexpected nature of this invention and highlights the great unpredictability associated with the preparation of hydrophilic polyolefinic microporous materials having desirable retention of their hydrophilic properties.

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EXAMPLE II

Following procedures similar to Example I, a series of hydrophilic Celgard 2400 polypropylene microporous films were prepared by immersing the microporous substrate films in an ultrasonic bath of various 60/40 methanol-water surfactant solutions, each of which contained identical concentrations of surfactant. The surfactants used for these tests included Igepal 510, 610 and 630 and Pluronic L43, F68 and L61. Immersion times ranges from 15 to 20 minutes.

Similarly to the results of Example I, the films  
treated with surfactants within the scope of this invention,  
the Igepals, exhibited excellent wet through characteristics,  
whereas films treated with the Pluronic surfactants were  
5 found not to be wettable.

The principles, preferred embodiments and modes of  
operation of the present invention have been described in  
the foregoing specification. The invention which is intended  
to be protected herein, however, is not to be construed as  
10 limited to the particular forms disclosed since those are  
to be regarded as illustrative rather than restrictive.  
Variations and changes may be made by those skilled in the  
art without departing from the scope of the invention as  
defined in the claims.

CLAIMS

1. A hydrophilic polyolefinic microporous material comprising a normally hydrophobic polyolefinic open-celled microporous substrate impregnated with an amount, sufficient to render the hydrophobic polyolefinic microporous substrate wettable with aqueous solutions, of at least one non-ionic surfactant of the class of alkylphenoxy poly(ethyleneoxy) ethanol compounds having an HLB in the range from 10 to 15.
2. The hydrophilic polyolefinic microporous material of claim 1, wherein the hydrophobic polyolefinic microporous substrate has a reduced bulk density as compared with the bulk density of a corresponding non-porous polyolefinic material, a crystallinity of at least 30 percent, an average pore size from 100 to 5000 Angstroms, a porosity from 40 to 90%, and a surface area of at least  $10 \text{ m}^2/\text{gram}$ .
3. The hydrophilic polyolefinic microporous material of claim 2 wherein the microporous substrate has a crystallinity from 50 to 100 percent and a surface area from 20 to  $100 \text{ m}^2/\text{g}$ .
4. The hydrophilic polyolefinic microporous material of any of claims 1 - 3 wherein the material impregnated with the surfactant has an electrical resistance less than 15 milliohms -  $\text{in}^2$ .
5. The hydrophilic polyolefinic microporous material of any of claims 1 - 4 wherein the microporous substrate comprises a microporous film or hollow fibre.
6. The hydrophilic polyolefinic microporous material of any of claims 1 - 5 wherein said surfactant has an HLB from 12 to 13.
7. The hydrophilic polyolefinic microporous material of any of claims 1 - 5 wherein the hydrophobic microporous substrate is impregnated with the surfactant in an amount sufficient to provide a surfactant add-on of 10 to 15% by weight.
8. A hydrophilic polyolefinic microporous material comprising a hydrophobic polyolefinic open-celled microporous substrate having a reduced bulk density as compared with the bulk density of a corresponding non-porous polyolefinic material, a crystallinity from 50 to 100 percent,

an average pore size from 100 to 5000 Angstroms, a porosity from 40 to 90% and a surface area from 20 to 100 m<sup>2</sup>/g, impregnated with a non-ionic surfactant of the class of alkylphenoxy poly(ethyleneoxy) ethanol compounds having an HLB in the range from 12 to 13 in an amount sufficient to provide a surfactant add-on of 10 to 15% by weight.

9. A method for preparing the hydrophilic polyolefinic microporous material of any of claims 1 - 8 comprising contacting the polyolefinic open-celled microporous substrate with the surfactant in the form of a solution in which the solvent is a solvent mixture comprising from 55 to 65 volume percent of methanol or acetone and from 35 to 45 volume percent of water whereby the polyolefinic microporous substrate is rendered wettable with aqueous solutions.

10. The method of claim 9 wherein the surfactant solution comprises from 1 to 10% by weight of the surfactant in an approximately 60:40 volume percent methanol to water or acetone to water solvent mixture, and the polyolefinic microporous substrate is contacted with the solution so as to provide a surfactant add-on of 10 to 15% by weight.